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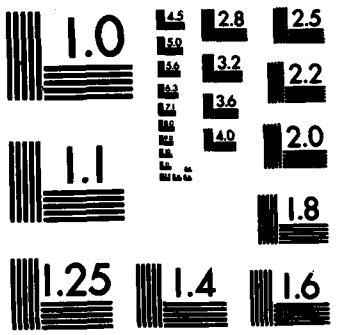

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TECHNICAL REPORT NO. 10

A Parallel Simulation Scheme for the Rapid Accurate Calculation of Nonideal Electrochemical Transients

by

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SUMMARY

A method for the digital simulation of certain electrochemical transients has been developed which involves the parallel calculation of a system of interest and an ideal analog to which an exact solution is available. A reduction in computer time of several orders of magnitude is realized compared to conventional simulations.

INTRODUCTION

Digital simulation of electrochemical experiments has been commonly used for a number of years now (1,2) when the complexity of the relevant equations prevents a closed-form solution of Fick's laws of diffusion. The information derived from these simulations is often qualitative in nature; for example, the effects of various electrode reaction mechanisms on the shapes of current, charge, and absorbance responses in potential-step experiments have been studied (3). There are cases for which it would be desirable to obtain more accurate data, however, such as applying the technique in the calculation subroutine of a nonlinear regression program. Limitations on the accuracy of the simulation often prevent this because such highly accurate solutions take much too long to execute to be of any practical value. This communication presents a method which can overcome this limitation and allow accurate digital simulations of certain systems with only a modest consumption of computer time.

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Such digital simulations involve a numerical solution of Fick's laws of diffusion with initial and boundary conditions appropriate to electrochemical experiments. Errors due to the approximate nature of the solution are not random noise, but occur as subtle changes in the shape of the simulated transient. This inaccuracy can be overcome by increasing the precision of the calculation and expending larger amounts of computer time, but this often is not practical on a routine basis. Therefore, under the common constraint of a limited amount of computation time, the exact shape of the simulated transient can depend markedly on the various simulation parameters employed (distance increment Δx, time increment Δt, etc.).

The procedure described here is best suited to systems which show relatively moderate deviations from some ideal behavior. A closed-form solution must be available for the ideal system. An example of such an application is the simulation of iR drop effects in normal pulse polarography, as it is possible to generate polarograms directly using an explicit solution when there is no uncompensated resistance (the ideal case). Other examples of electrochemical nonidealities to which the method can be applied include instrumental deviations (finite potentiostat rise time), chemical effects (bulk solution kinetics or reactant adsorption), and geometric effects (shielding by capillaries or edge effects). Of course, there are similar potential applications in other areas, for example in heat transfer.

OUTLINE OF METHOD

The scheme which has been developed involves parallel simulations of the nonideal system of interest and an ideal system to which a closed-form

solution is available. The calculations share all simulation parameters, and are identical except for the boundary conditions describing the nonideality. Thus, two transients are produced, each with about the same amount of error from the simulation process itself, so that any differences between them are due almost entirely to the effect of the nonideality. Since the exact, calculated transient is available for the ideal case, it is possible to impress the observed deviations from ideality on the calculated curve to yield a transient which shows a minimum of influence from simulation errors, and which accurately reflects the effect of the nonideality. This parallel simulation process can be summarized as follows:

$$X_{\text{nonideal}}^{\text{calculated}} = X_{\text{ideal}}^{\text{calculated}} \left(\frac{X_{\text{nonideal}}}{X_{\text{ideal}}} \right)_{\text{simulated}} \qquad (1)$$

where X is a measured quantity (current, overpotential, etc.) which is generally a function of time.

It is important to select an ideal function which is as similar as possible to the nonideal system of interest; the greater the difference between the parallel simulations, the more the inaccuracies of the simulation will influence the result. Additionally, both simulations should be of the same general type (explicit finite-element, etc.).

EXAMPLE SYSTEM

An illustrative example of the use of this procedure will now be presented. In practice, it is difficult to test the accuracy of a simulation because an exact solution to the problem is not available. For this example, however, a nonideal experiment was chosen to which a closed-form solution has been derived, allowing the performance of the new method to be assessed quantitatively.

An equation has been derived (4) for a potential-step experiment involving a quasi-reversible electrode reaction in which the potential rises linearly in time from the initial to the final value. This will be the "nonideal" system in this example. The equation for the same experiment with an instantaneous potential step is well known (5); this will serve as the ideal system. The simulations were explicit finite-difference calculations with distance increments Δx_i that expand exponentially with increasing distance from the electrode surface. No further optimizations were used, and only single precision arithmetic was employed. For the calculations of the ideal and nonideal transients, it is necessary to evaluate the exponential error function complement,

$$f(x) = \exp(x^2)\ \mathrm{erfc}\ (x) \qquad (2)$$

A rational function approximation developed by Flanagan (6) was used for this purpose.

Parallel simulations of an ideal, instantaneous potential-step experiment and a linearly rising (nonideal) potential-step experiment were performed. A number of data points were collected along the transients at regular intervals after the potential achieved the desired value. The exact time of each point, the nonideal current at that time, and the corresponding ratio of the nonideal to ideal currents were recorded. These ratios were then combined with the calculated ideal values to yield a "calculated nonideal" transient using Eqn. (1).

The accuracies of the "calculated nonideal" and the conventionally simulated transients were evaluated as follows. The currents, i_{sim}, along these two simulated transients were compared to the corresponding currents on the explicitly calculated nonideal transient, i_{exact}, and a standard deviation of simulation σ_{sim} was calculated:

$$\sigma_{sim} = \left(\frac{\Sigma(i_{sim} - i_{exact})^2}{n} \right)^{\frac{1}{2}} \qquad (3)$$

as a measure of the error in each of the simulation procedures.

Figure 1 is a plot of the standard deviation as a function of the simulation parameter Δx_1 for a typical transient. The time increment Δt was also varied so that the quantity $\Delta tD/\Delta x_1^2$, where D is the diffusion coefficient of the reactants, was held constant at 0.4. It is evident that the transient calculated by the parallel simulation scheme is affected to a much smaller extent by the varying simulation parameters than is the conventionally simulated curve. Since the limitation on simulation accuracy is generally computation time, the data in Fig. 1 have been replotted in Fig. 2 to show the error in the simulated transients as a function of computation time. (Note that the calculated nonideal transients take twice as long to execute due to the two parallel simulations; the time to calculate the ideal transient was negligibly short.) The advantage of the new method is now more apparent: execution time can be reduced by several orders of magnitude, even while producing more accurate simulations.

CONCLUSIONS

This savings in execution time results in obvious advantages in terms of routine applications of digital simulations on small laboratory computers, and in such time-demanding procedures as nonlinear regression. It also yields an added advantage in that it is no longer necessary to go to more complicated numerical methods to produce accurate simulations in a reasonable amount of time. Workers with only a minimum amount of mathematical expertise should have no difficulty with the simpler digital simulation routines.

This method has been used successfully in this laboratory in two ways. Experimental data are being fitted to more sophisticated model systems in

order to extract heterogeneous kinetics data from chronoamperometric transients which are distorted by one or more nonidealities. We are also studying the effect of chemical and instrumental nonidealities on the results of experiments designed to measure fast electrochemical reaction rates.

Not only is this method generalizable to other, related problems (heat transfer, etc.), but probably also to other types of numerical integration as well, although we have not investigated this. As long as there is a similar function available which can be calculated directly as well as integrated by the same method as the unknown function, this technique might prove useful for increasing the accuracy of the resulting function while lowering the amount of time expended in its computation.

ACKNOWLEDGMENTS

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FIGURE CAPTIONS

Figure 1 Standard deviation of simulation *vs.* simulation parameter Δx_1 for typical systems. Curve 1: conventional simulation. Curve 2: parallel simulation.

Figure 2 Standard deviation of simulation *vs.* computation time for typical systems. Curve 1: conventional simulation. Curve 2: parallel simulation.

FIG 1

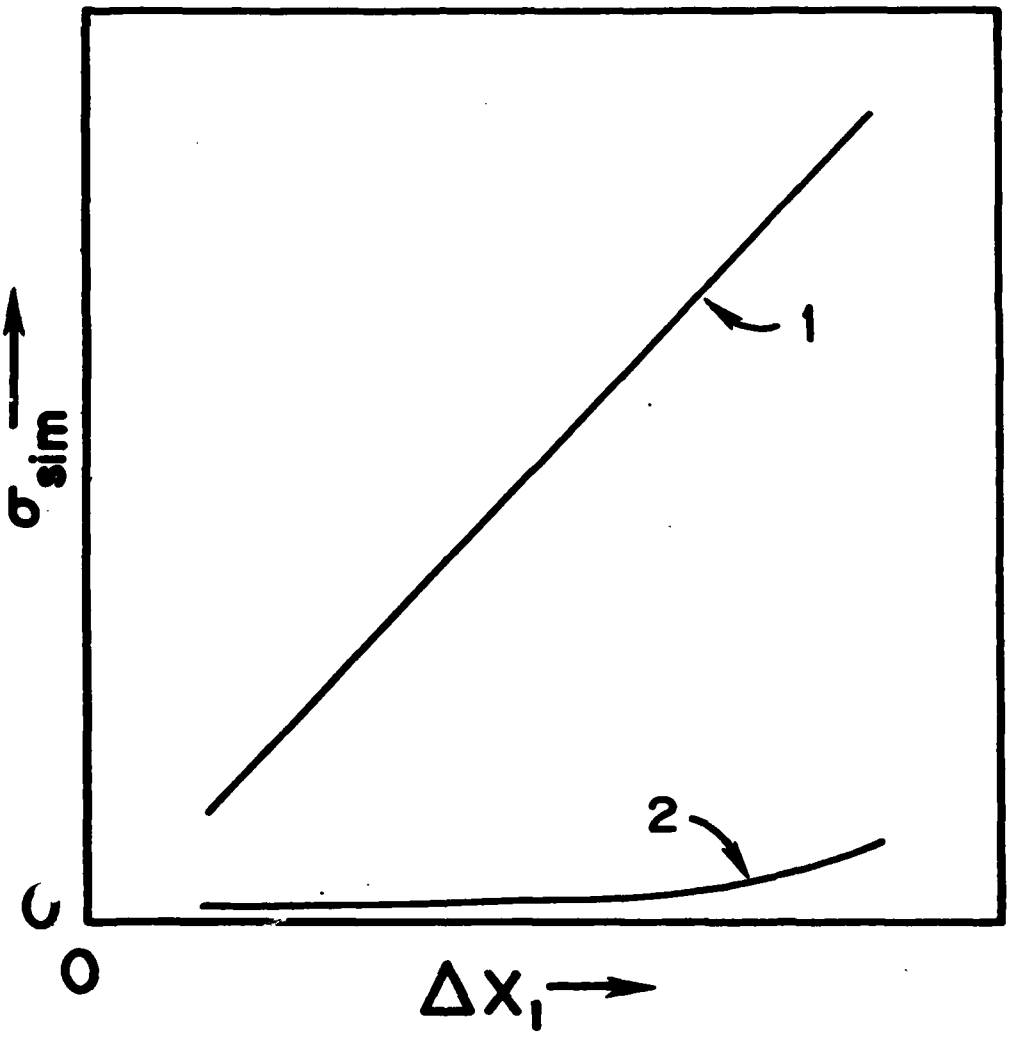
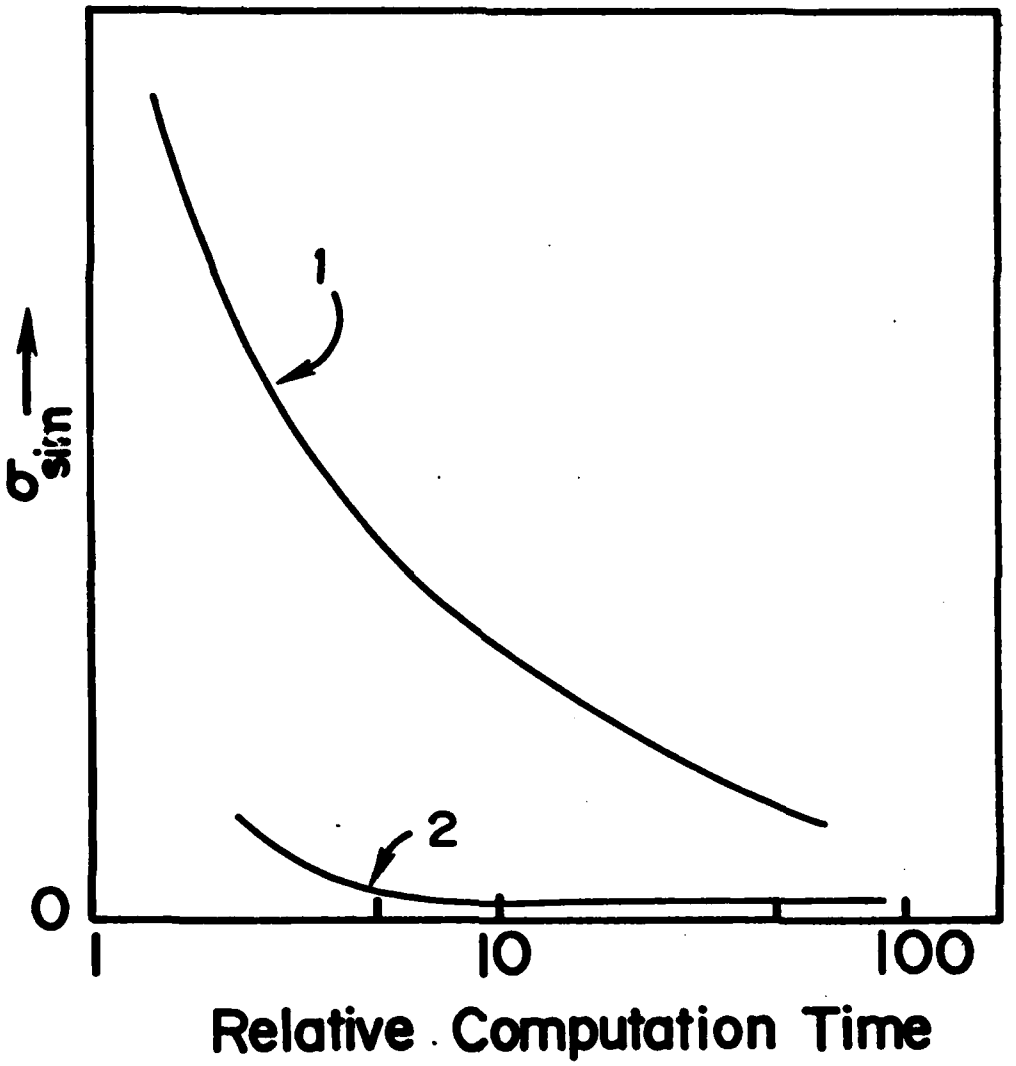
FIG 2